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Status of Research to Develop Acidic Dry Deposition Monitoring Capability

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16. ABSTRACT

Dry deposition is thought to be as important as wet deposition in acidifying ecosystems. However, at present acidic dry deposition of relevant particles and gases cannot be monitored directly in a quantitative manner. The U.S. EPA Workshop on Dry Deposition (Report No. EPA-600/9-80-050) recommended that dry deposition velocities be parameterized as a function of micrometeorology and surface type to permit the use of ambient pollutant concentration data for inferring dry flux ("concentration monitoring" technique). Also, the micrometeorological technique's variance, modified-Bowen ratio, and eddy accumulation were identified as candidates for development as dry flux monitors for network stations.

This approach has been adopted by the task group on "Deposition Monitoring of Acidic Substances" of the Interagency Task Force on Acid Precipitation. Research monitoring stations have been established at Oak Ridge, TN, Argonne, IL, and University Park, PA for the purpose of intercomparing "concentration monitoring", the three previously identified micrometeorological techniques, and eddy correlation. Intercomparison tests are being performed for SO_2, NO_2, HNO_3, NH_3, O_3, and particulate SO_4^{2-}, NO_3^-, and NH_4^+. The status of methods development and performance is presented.

SO4(-2), NO3(-1), and NH4(+1)

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Introduction

The United States Congress formed the Interagency Task Force on Acid Precipitation to establish a comprehensive research, monitoring, and assessment program to increase our knowledge and understanding of the causes and effects of acidic deposition.[1] The needs for information have been identified and assigned to nine research task groups for action: A. Natural Sources, B. Man-Made Sources, C. Atmospheric Processes, D. Deposition Monitoring of Acid Substances, E. Aquatic Impacts, F. Terrestrial Impacts, G. Effects on Materials and Cultural Resources, H. Control Technologies, and I. Assessment and Policy Analysis.[2]

There is a need for long-term wet and dry deposition monitoring to establish the present patterns and to reveal changes resulting from modifications of emissions. It is recognized that dry deposition rates of acids and acid precursors may equal or exceed the wet deposition rates.[3,4] Thus, no meaningful progress can be made in defining the total deposition patterns and changes until reliable dry deposition monitoring methods are developed and placed in the long-term routine monitoring networks.

Task Group D (Deposition Monitoring of Acid Substances) has identified several severe limitations in monitoring networks.[2] Those that are especially applicable to dry deposition monitoring are:

-- techniques and strategies used by scientists in the U.S. and other countries may be mutually inconsistent; and
-- methods for monitoring acidic dry deposition are inadequate.

The development of dry deposition monitors for defining trends in the acidification of ecosystems must consider the identity of the important chemical species and the type of surfaces in the ecosystems. The important chemical paths of ecosystem acidification are not yet established, but they should be anticipated to include the dry deposition of acidic gases (e.g., HNO_3), acidic particles (derived from H_2SO_4, HNO_3, carboxylic acids), acidic precursors (e.g., SO_2, NO_2, organic compounds), oxidants (e.g., H_2O_2, O_3, PAN), and basic compounds (NH_3, alkaline dust).

Acidic gases and particles that are dry deposited may act directly as acidifiers:

$$HNO_3 \xrightarrow[H_2O]{} H^+ + NO_3^- \quad (1)$$

$$H_2SO_4 \xrightarrow[H_2O]{} 2H^+ + SO_4^{2-} \quad (2)$$

$$RCOOH \xrightarrow[H_2O]{} H^+ + RCOO^- \quad (3)$$

The mineral acid precursors may dry deposit and then react to form strong acids. The oxidations of these precursors may result from metal (Mn^{2+},

Fe^{3+}) ion catalysis, reaction with a strong oxidant (H_2O_2, O_3), or action of oxidizing bacteria. For SO_2 and NO_2 dry deposited in excess of the nutritional needs of the surfaces, the following reactions are likely:

$$SO_2 \xrightarrow[H_2O]{} H^+ + HSO_3^- \quad (4)$$

$$HSO_3^- \longrightarrow H^+ + SO_3^{2-} \quad (5)$$

$$HSO_3^- \xrightarrow{\text{oxidation}} H^+ + SO_4^{2-} \quad (6)$$

$$SO_3^{2-} \xrightarrow{\text{oxidation}} SO_4^{2-} \quad \text{(unbalanced)} \quad (7)$$

$$NO_2 \xrightarrow[H_2O]{\text{reduction}} HNO_2 \quad \text{(unbalanced)} \quad (8)$$

$$HNO_2 \xrightarrow{\text{oxidation}} H^+ + NO_3^- \quad \text{(unbalanced)} \quad (9)$$

The oxidants that are dry deposited may undergo reactions with either naturally occurring S, N, or organic compounds or those co-deposited to form acids. The role of oxidants as acidifying agents in terrestrial and aquatic systems has not yet received attention, and their importance is not known. The reactions that are likely to be important are:

$$\left|\begin{matrix} H_2O_2 \\ O_3 \\ PAN \end{matrix}\right| + \left|\begin{matrix} H_2S,\ H_2SO_3 \\ HNO_2 \\ \text{organics} \end{matrix}\right| \longrightarrow \left|\begin{matrix} H_2SO_4 \\ HNO_3 \\ RCOOH \end{matrix}\right| \quad \text{(unbalanced)} \quad (10)$$

However, not all oxidant reactions in terrestrial and aquatic systems result in acid formation. Oxidants may also be formed directly in surface waters, especially if contaminated with organic compounds and subjected to sunlight.[5]

The important chemistry of the basic gaseous and particulate compounds is to neutralize the strong acids through reactions such as:

$$NH_3 + H^+ \longrightarrow NH_4^+ \quad (11)$$

$$CaCO_3 + H^+ \longrightarrow Ca^{2+} + HCO_3^-. \quad (12)$$

Therefore, the likely species that influence the rate of acidification of terrestial and aquatic systems are expected to include those identified in Table I. Monitoring the dry deposition of these species presents a challenge that exceeds a simple extension of present capabilities in micrometeorology and analytical chemistry.

This problem was anticipated and was the topic of an Environmental Protection Agency workshop on dry deposition.[6] Among the recommendations

TABLE I. CHEMICAL SPECIES THAT CONTRIBUTE TO ECOSYSTEM ACIDIFICATION

GASES				PARTICLES	
Acids	Base	Precursors	Oxidants	Fine (diam. < 2-3 μm)	Coarse (diam. > 2-3 μm)
HNO_3	NH_3	SO_2	H_2O_2	H_2SO_4	$CaCO_3$
HCl		NO_2	O_3	HNO_3	$MgCO_3$
HNO_2			PAN	$(NH_4)_2SO_4$	
RCOOH				NH_4NO_3	
				RCOOH	

of the workshop that relate to the development of a dry deposition monitoring capability are:

1. We should not continue to rely on the dry dust bucket for acidic dry deposition monitoring.

2. Alternative techniques should be developed for use as direct dry deposition monitors. Possible micrometeorological methods include (a) variance, (b) modified Bowen ratio, and (c) eddy accumulation. Development of surrogate surfaces was also recommended, although this was a subject of some dissention.

3. Work should be encouraged to parameterize dry deposition velocities for use in estimating dry deposition through monitoring of pollutant concentrations at acceptable sites and conditions.

The third recommendation offers an interim approach to monitor dry deposition until direct monitors are developed. The parameterization of the dry deposition velocities is also the approach being taken by scientists in Europe and in Canada.

Description of Methods

Dry deposition is the net downward migration of mass through the air, followed by sorption, chemical reaction, or physical attachment to the earth's surface. In situations in which concentrations are not changing rapidly with either time or distance, the flux F of material through the layer of constant flux adjacent to the earth's surface may be written as

$$F = -K_z(dC/dz) \tag{13}$$

where

F = flux, mass/length^2/time
K_z = the vertical eddy diffusivity, length^2/time
C = the concentration of the migrating material, mass/length^3
z = height above the surface, length.

By convention, turbulent fluxes directed towards the earth's surface have a negative sign, and the associated deposition velocity v_d (defined as the ratio -F/C) is positive. There are several micrometeorological methods by which fluxes can be measured within this zone of constant flux. Eddy correlation methods developed in earlier studies of the transfer of moisture, heat, and momentum have been modified to evaluate the flux of non-settling pollutants for which sufficiently rapidly responding sensors are available. This method evaluates the vertical flux as the average product $\overline{w'C'}$, where w is the instantaneous vertical wind velocity and where primes denote departures from mean values. Eddy correlation is technologically demanding, and its application is severely limited by the requirement for sensor response times typically extending to less than 1 Hz.

Gradient methods are a direct application of equation (13). They require the accurate measurement of vertical concentration differences that are almost always less than 10%, and they assume that independent evaluations of the appropriate diffusivity K_z are available. Both requirements impose technological obstacles that are often difficult to overcome. Thus, it has become apparent that neither of these research-oriented micrometeorological methods is likely to be suitable for deposition monitoring on a routine basis.

Difficulties also exist with the use of surrogate surfaces, although these are also in fairly widespread use in intensive research programs. Surrogate surfaces cannot provide easily interpretable information on the deposition of trace gases, and even in the case of small particles it is not clear that they reproduce the deposition and capture characteristics of natural surfaces. That is because the physiology and morphology of surrogate surfaces do not correspond to natural surfaces. Work is proceeding, therefore, on the improvement of both micrometeorological and surrogate surface methods for measuring dry deposition. The following comments are intended to explain some of the possibilities that are currently being evaluated.

Measurement Methods

Variance. Turbulent transfer through the constant flux layer is characterized by velocity and concentration fluctuation variances that are fairly well understood.[7] Concentration variance at high frequency is directly related to the flux of the material in question; however, the precise relationship is also known to involve atmospheric stability, wind speed, and other meteorological variables. Methods for evaluating pollutant fluxes from records of concentration variance are presently being investigated.

Modified Bowen Ratio. If some other turbulent flux can be measured directly, then the flux of pollutant can be inferred by relating some characteristic of the pollutant concentration field with the same characteristic feature associated with the known flux. This approach is an extension of a procedure developed in agrometeorology, which assumes that the ratio of sensible heat flux to latent heat flux (H/LE, defined as the Bowen ratio)

is proportional to the ratio of vertical gradients of potential temperature and specific humidity, $(d\theta/dz)/(dq/dz)$. If the vertical diffusivities of heat and moisture are the same, then the constant of proportionality is determined by the specific heat of air and the latent heat of vaporization of water. The so-called modified Bowen ratio method proposes to extend this general approach to the case of pollutant exchange by relating the quantity H/F to the gradient ratio $(d\theta/dz)/(dC/dz)$.

Eddy Accumulation. Standard eddy correlation procedures involve the use of fast-response anemometers and pollution sensors. The requirement for a rapid response pollution concentration sensor can be bypassed if sufficiently accurate sampling apparatus can be arranged, so that pollutant concentrations can be accumulated (as on a filter, for example) at a volumetric sampling rate proportional to the instantaneous vertical velocity. The use of two such systems, one active during updrafts and the other during downdrafts, would permit the eddy flux to be evaluated from the difference in pollutant loadings accumulated by the two systems. The technique has been demonstrated for sensible heat[8], but application to the case of a slowly depositing material has yet to be successful.

Surrogate Surfaces. In some situations, the accumulation of pollutants on surfaces can be measured directly. For example, dry deposition rates of some pollutants to building materials can be determined by measuring the accumulation of chemical products on passive samplers of that material. Also, deposition rates can be estimated from the change in mass of the passive sampler. Surrogate surfaces offer similar advantages, yet suffer from the difficulty that they do not have the same physiology and morphology as the natural surfaces that are of major interest. However, surrogate surfaces are sometimes capable of providing more detailed information than can be derived from alternative methods. That is the case, for example, in studies of the distribution of dry deposition flux within vegetated canopies or among buildings.

The efforts to develop the preceeding methods have the aim of extending existing techniques to provide more accurate evaluations of dry deposition fluxes, both on a routine basis for direct network application and on a case basis for use in studies of the processes that control dry deposition. Such case studies provide the basic information necessary to evaluate pollutant-specific deposition velocities as functions of time and space. If sufficient knowledge of the deposition velocities were available, then it would no longer be necessary to measure deposition fluxes directly, since the fluxes could be evaluated from measurements of atmospheric pollutant concentration and supporting data. It is this concentration monitoring protocol that is the basis of plans to initiate dry deposition monitoring.

Concentration Monitoring Methods

The deposition velocity appropriate for any of the pollutants discussed previously will vary considerably with both time and space. Meteorological, physiological, and morpological factors are likely to be important. Factors

such as wind speed, atmospheric stability, stomatal resistance, and soil water status impose a strong diurnal variability that is a feature of heat and water vapor exchange, as well as of pollutant deposition. Moreover, deposition velocities will vary from surface to surface. For example, SO_2 deposition velocities to stone are affected by surface chemistry,[9] whereas SO_2 deposition velocities to vegetation are often controlled by stomatal resistance.[10] A first estimate of pollutant dry deposition rate can be obtained by applying an average deposition velocity to average concentration data obtained over some long sampling interval, but clearly it would be preferable to take such factors as diurnal variability into account. More accurate answers might be based on concentrations measured hour-by-hour, using deposition velocities calculated with the same time resolution. At this time, the necessary cost/benefit calculations have not been completed; however, the elucidation of the most appropriate sampling protocol for concentration measurement and for deposition velocity determination will be a major product of this research program. There are several alternative sampling methods that have been used successfully. These lie between the extremes representing intensive analysis of very short-term concentration data to application of suitably weighted-average deposition velocities to long-term concentration averages.

It is of immediate relevance to specify the goal of any such monitoring program in some detail, since this will help guide the process by which a suitable sampling protocol will be selected. The intent is to provide a listing of dry deposition rates of the pollutants presently considered in wet deposition programs, with the same time resolution: one week. Among the many alternative suggestions that have been put forward, the following are receiving special attention.

Weekly Sampling. The use of filter packs or some similar procedure to provide data on weekly average concentrations by direct chemical sampling has the benefit of reducing analysis costs to the lowest possible level. However, it requires that suitably weighted-average deposition velocity data are available.

Daily Sampling. Some concentration-monitoring networks have adopted a daily-sampling protocol in order to resolve the variability associated with pollution episodes and changing weather. Such data could be combined with day-by-day evaluations of appropriate deposition velocities to form the average deposition fluxes that are required. The expanded detail is at the expense of more frequent analysis and necessitates more detiled deposition velocity information.

Day/Night Sampling. It is known that deposition velocities at night are substantially less than in daytime;[11] Therefore, it has been suggested that much of the uncertainty associated with weekly sampling could be reduced by using two samples, one for night and the other for daytime operation, with deposition velocities calculated accordingly. This suggestion has yet to be evaluated.

Stability-Decoupled Sampling. The day/night variation mentioned above is largely a consequence of effects associated with atmospheric stability,

which can become sufficiently great at night that dry deposition is reduced to an insignificant level (relative to daytime, unstable rates), with the possible exception of settling particles. A suggestion that concentration sampling should be confined to those periods during which deposition is occurring, as indicated by some independent indicator of stability, is presently under consideration.

The four alternative monitoring protocols listed above are not the only suggestions that have been made; however, they give an indication of the range of options that are available. An immediate goal of the dry deposition monitoring program is to select the optimum sampling methodology, and to test it at a few carefully selected sites. Work to address this question is presently in progress at experimental research monitoring sites near State College, PA; Argonne, IL; and Oak Ridge, TN.

Summary

Following initial recommendations of an EPA-sponsored workshop on dry deposition monitoring, work is progressing on two parallel fronts. One effort intends to lead to the development and eventual deployment of direct monitoring instruments for dry deposition rates of gaseous and particulate pollutants to natural surfaces, using techniques that do not interfere with the natural uptake characteristics of the surfaces themselves. The second effort addresses the need to initiate indirect "concentration monitoring" as a means to estimate dry deposition rates on a routine basis. Experiments conducted to test and compare methods for measuring dry deposition serve the purposes of both approaches. They provide the deposition velocities needed in conjunction with the concentration measurements. They also provide the opportunity to test new techniques for measuring deposition by a wide range of methods, not necessarily limited to the micrometeorological methods that have been discussed here.

The present aims are to deploy concentration monitoring devices at selected locations in the immediate future, in order to test the alternative monitoring protocols as well as to evaluate the performance of the monitoring devices themselves. Methods for evaluating direct pollutant-specific and location-dependent deposition velocities will also be developed.

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